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Growth mechanism, field emission and photoluminescence property of Ge-doped hexagonal cone-shaped GaN nanorods

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ABSTRACT

The Ge-doped hexagonal cone-shaped GaN nanorods have been synthesized by the VLS process. The variation of N-rich condition and Ga-rich condition in reaction chamber results in the morphology of the Ge-doped GaN nanorods being hexagonal cone-shaped. The Ge-doped hexagonal cone-shaped GaN nanorods exhibit an excellent emission property with typical turn-on electric field as low as 2.93 V/μm, this indicates that the Ge-doped hexagonal cone-shaped GaN nanorods could be well used in cold cathode electron source applications. The photoluminescence spectrum of the Ge-doped hexagonal cone-shaped GaN nanorods indicates it could be applied in blue-violet and ultraviolet photoelectric devices.

1. Introduction

Gallium nitride (GaN) is an excellent candidate material for short wavelength optoelectronic devices, such as light-emitting diodes (LEDs), laser diodes (LDs), and cathode material of field emission (FE) devices on account of its direct and wide band-gap of 3.4eV, low work function (4.1 eV), low electron affinity (2.7–3.3 eV), high chemical and physical stability, and a higher melting point (1500 °C) [1,2]. For semiconductor materials, the FE properties mainly depend on the work function, morphology, dimension, and the apex geometry of one-dimensional (1D) nanomaterials. The morphologies of synthesized 1D GaN nanostructure in recent years are various, such as nanobelts , nanowires , nanorods , and nanotubes, etc. For example, prismatic sub-micro rods and cone GaN nanowires [3], grass-like GaN nanostructures [4], needle-like bi-crystalline GaN nanowires [5], GaN nanobelts with herringbone [6], triangular GaN nanowires [7], P-doped triangular GaN microtubes [8], well-aligned GaN nano-columns [9], needle-like GaN nanowire arrays [10], GaN nanotowers [11], and conical shape GaN nanorods [12] have been synthesized successfully. Some of them have excellent FE properties on account of their special morphologies. Doped impurity can enhance the electrical, optical, and magnetic properties of GaN, and GaN is frequently doped with In, Ge, Si, Mg, Al, Zn, Mn , and Fe [13–23]. Thus far, in addition to the physical properties of Ge-doped bulk GaN, the physical properties of Ge-doped 1D GaN nanostructures have also been studied [24–26].

In this study, Ge-doped hexagonal cone-shaped GaN nanorods have been synthesized on Si (111) substrates by a direct reaction between Ga_2O_3 and ammonia gas using an Pt catalyst in a chemical vapor deposition (CVD) reactor. The tips of the GaN nanorods containing the Pt catalyst particle marks growth mechanism as VLS. HRTEM and XRD analysis indicate that GaN nanorods have a preferential crystal structure and the growth direction is along the c-axis. The as-synthesized conical shaped GaN nanorods have exhibited tremendous field emission properties with a turn-on field of 2.93 V/μm (at a current density of 0.01 mA/cm^2) and high emission stability at room temperature which is sufficient for application in field emission displays and vacuum nanoelectronic

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devices. The cone-shaped tips, high density, and smaller tip radii of curvature of the GaN nanorods make them exhibit excellent field emission properties. The PL property of the Ge-doped GaN nanorods in room temperature has been showed also.

2. Experiment procedure

Ge-doped hexagonal cone-shaped GaN nanorods were synthesized by thermal CVD in tube furnace. The Ga_2O_3 powder and a small amount of GeO_2 were placed on the upstream side of the alumina boat 1 cm and 3 cm away from the Pt catalyst nanoparticles coated Si (111) substrate, respectively, and the alumina boat was located in the center of the quartz tube of a horizontal evaporation system. High-purity N_2 (99.99%) and NH_3 (99.99%) were introduced into the reactor as carrier and reaction gases, respectively. N_2 was introduced into the quartz tube at a flow rate of 1000 sccm while the furnace was heated at a ramp rate of 10 °C min^{-1} to reach the required temperatures (800 °C and 1150 °C). NH_3 was introduced at a flow rate of 200 sccm for 10 min at 800 °C, the main growth of the GaN nanostructures were carried out for 30 min at 1150 °C, while NH_3 at a flow rate of 350 sccm. After the main growth phase, the samples were cooled naturally, when the temperature was 700 °C maintaining for 30 min, then to room temperature.

The shape and morphology of the GaN nanostructures have been observed by scanning electron microscopy (SEM). The crystalline structure of the GaN nanostructures has been examined by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The chemical composition has been investigated using energy dispersive spectrometer (EDS). Photoluminescence (PL) property at room temperature has been studied using the PL spectrum with a Fluorescence Spectrophotometer (F-4500). The field emission property has been investigated in a vacuum chamber with a pressure of 3.8×10^{-4} Pa at room temperature.

3. Results and discussion

SEM images of Ge-doped GaN nanorods (Fig. 1, (a) to (c) are the low to high magnification) show that GaN nanorods grow at an angle with silicon substrate and with a uniform density on the substrate. The lower parts of the most nanorods show transverse-nodular texture, and except for a very few, the most top parts are conical hexagonal prism with smooth surface. The total length of nanorods is less than 10 μm, and the diameter is less than 500 nm. In addition, it can be seen from Fig. 1 (c), there is Pt catalyst at the end of the nanorod indicating the growth mechanism of the GaN nanorods in this study is based on VLS mechanism , and the top cross section is hexagonal.

The XRD pattern of the Ge-doped hexagonal cone-shaped GaN nanorods is shown in Fig. 2, the diffraction pattern indicates that the sample exhibits a hexagonal wurtzite GaN crystal structure with lattice constants of $a = 0.3189$ nm and $c = 0.5185$ nm, in agreement with the standard values of bulk GaN crystal. It is noteworthy that the diffraction pattern of the Ge-doped hexagonal cone-shaped GaN nanorods exhibites a noticeably strong peak (002) plane, which can confirm that a great portion of the Ge-doped hexagonal cone-shaped GaN nanorods are preferred along the c-axis. The diffraction peaks caused by the metallic Ge or a secondary phase are not observed.

EDS image in the inset of Fig. 2 confirms that the composition of the nanorods is Ga, N, and Ge, and the Ge content is about 1.6 at %. However, the diffraction peaks of Ge and its compounds do not appear in the XRD pattern, indicating that impurity doping is effective. The spectra of EDS obtained from different nanorods are almost the same, which shows that more nanorods in the samples have been effectively doped with Ge impurity.

Fig. 3 displays the HRTEM image for a certain small areas of a Ge-doped hexagonal cone-shaped GaN nanorod in Fig. 1 (c). The HRTEM image reveals the lattice fringes with interplanar spacings of 0.25 nm, corresponding to the (002) planes of wurtzite GaN. Therefore it can be confirmed that the GaN nanorod grows along the *c*-axis, consistent with the XRD results. The selected area diffraction (SAD) pattern reveals the GaN nanorod is with single crystal wurtzite structure.

Different growth rates of GaN crystal planes result in the variation of cross section diameter of the GaN nanorod. The (0001) crystal plane represents the polarity, and during the growth process, Ga-rich condition leads to higher lateral growth rate than axial growth rate, while the N-rich condition results in higher axial growth rate than lateral growth rate. In the initial stage of the reaction, minor periodic changes of the Ga-rich and N-rich conditions cause the periodic transverse-nodular texture in the lower part of the most nanorods, while the diameter is almost constant. During the whole growth process, the constant flow of NH_3 provides N source, but Ga source is decreasing, especially at the later stage in the growth process, so the reaction environment is N-rich condition and the amount of Ga atom is less and less in a smooth tapered shape with decreasing diameter at the end of the nanorods. The surface energy of (0001) and (1–100) planes are smaller, so growth rates of these two surface are faster. Growth rate along [0001] direction is faster resulting in the hexagonal prism shape cross-section with (0001) and (1–100) planes along the [0001] growth direction.

Fig. 4 (a) shows the field emission J-E curve of the Ge-doped hexagonal cone-shaped GaN nanorods, the inset is the corresponding F-N curve. It can be seen, the open electric field of the Ge-doped hexagonal cone-shaped GaN nanorod is as low as 2.93 V/μm (at a current density of 0.01 mA/cm^2). The linearity of the inset F-N curve shows the electron emission of the Ge-doped hexagonal cone-shaped GaN nanorods belongs to field-induced electron emission. The field emission current stability of the Ge-doped hexagonal cone-shaped GaN nanorods within 1 h under the applied electric field of 5.5 V/μm is shown in Fig. 4 (b), the initial current density and the average current density are 158.1 $\mu A/cm^2$ and 155.7 $\mu A/cm^2$, respectively. No obvious current density change is observed and the fluctuation of the emission current is as low as 1.52%, indicating that the Ge-doped hexagonal cone-shaped GaN nanorods have excellent field emission stability.

The Ge-doped hexagonal cone-shaped GaN nanorods exhibit excellent field emission properties due to the cone-shaped tips, high density, smaller tip radii of curvature of the GaN nanorods and two following points: (1) The surfaces of the lower parts of the GaN